Alternative to Nitric Acid Passivation Project Overview

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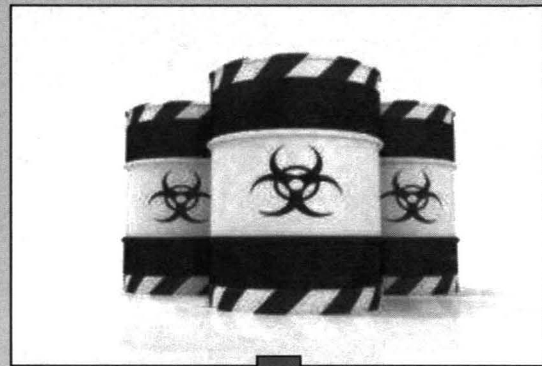
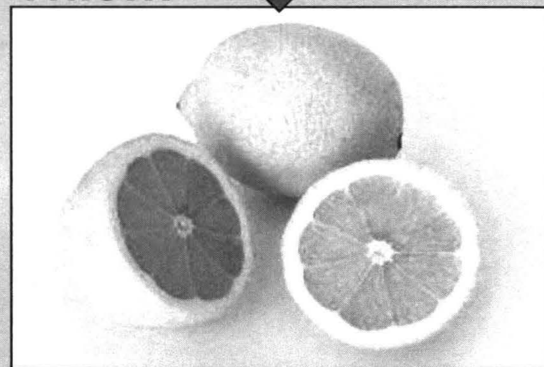


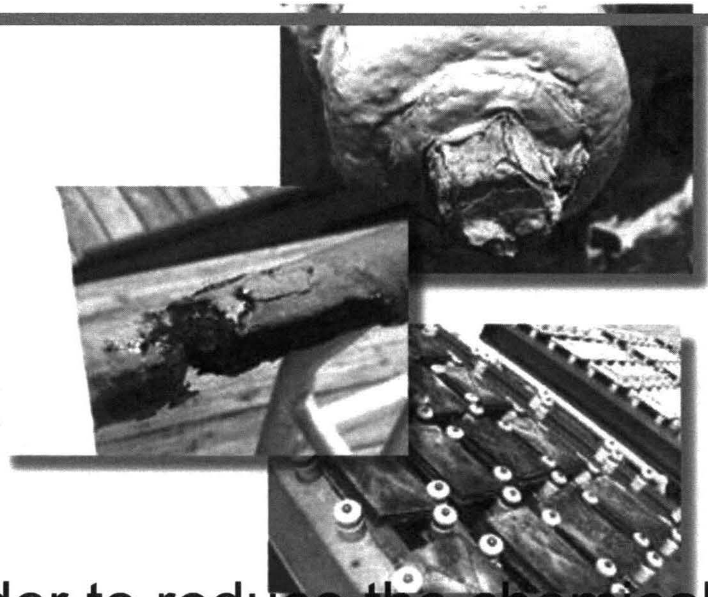
To This…



Project Team Members

1. **NASA**
   - Ground Systems Development and Operations Program
   - NASA TEERM Principal Center
   - NASA Corrosion Technology Laboratory
   - Kennedy Space Center, Marshall Space Flight Center, Stennis Space Center, White Sands Test Facility, Johnson Space Center, Goddard Space Flight Center, and Wallops Flight Facility
2. **U.S. Department of Defense**
   - Army
   - USMC
   - Air Force
   - Navy
3. **European Space Agency (ESA)**
   - ESTEC
   - Guiana Space Centre

Background



1. **Corrosion is expensive**
   - Financial
   - Asset Downtime
   - Worker Safety
   - Environmental Risks
2. **Passivation**
   - To treat or coat (a metal) in order to reduce the chemical reactivity of its surface.
   - Process forms a shielding metal oxide layer reducing the impact of deleterious environmental factors (i.e. air, water, etc.).
3. **Specification QQ-P-35C**
   - Details the specific passivating processing conditions for stainless steels using nitric acid.
   - Used extensively by the military and industry, but has been cancelled.

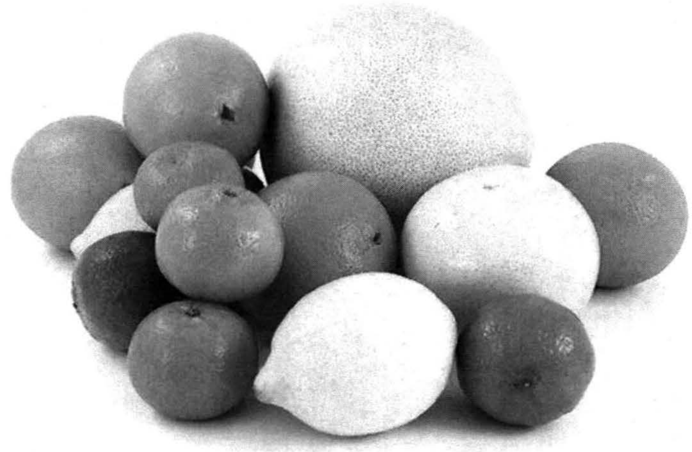
Drawbacks of Nitric Acid

1. **Air Pollution**
   - Nitrogen Oxide (NOx) Emissions are considered Greenhouse Gases (GHGs) and Volatile Organic Compounds (VOCs)
   - Subject to Federal and State Regulations
2. **Wastewater**
   - Regulated under Metal Finishing Categorical Standards
   - Local wastewater treatment facility may also require permits or pretreatment
3. **Worker Safety**
   - NOx Emissions are toxic to workers
   - Passivation tanks require local exhaust ventilation or general area ventilation
4. **Operational**
   - Can remove beneficial heavy metals that give stainless steel its desirable properties

Benefits of Citric Acid

1. Bio-based Material—meets requirements of

- Farm Security and Rural Investment Act of 2002
- EO 13423
- EO 13514



2. No Toxic Fumes

- Safer for workers
- Less required ventilation

3. Improved Performance

- Citric acid removes free iron from the surface more efficiently
- Requires lower concentrations
- Processing baths retain potency better requiring less frequent refilling
- Reduced volume and potential toxicity of effluent and rinse water

4. Lower Costs

Previous Work

2008 – United Space Alliance (USA) asked to evaluate citric acid as a replacement for nitric acid in passivating baths.

- **USA began work with 2 objectives:**
  - Investigate corrosion resistance afforded by citric acid passivation.
  - Optimize processing parameters for the process.
- **USA looked at the following alloys:**
  - UNS S30400 Austenitic
  - UNS S41000 Martensitic
  - UNS S17400 Precipitation-Hardened Martensitic

Conclusion: ***Citric acid most likely performs as well as, or better than, nitric acid.***

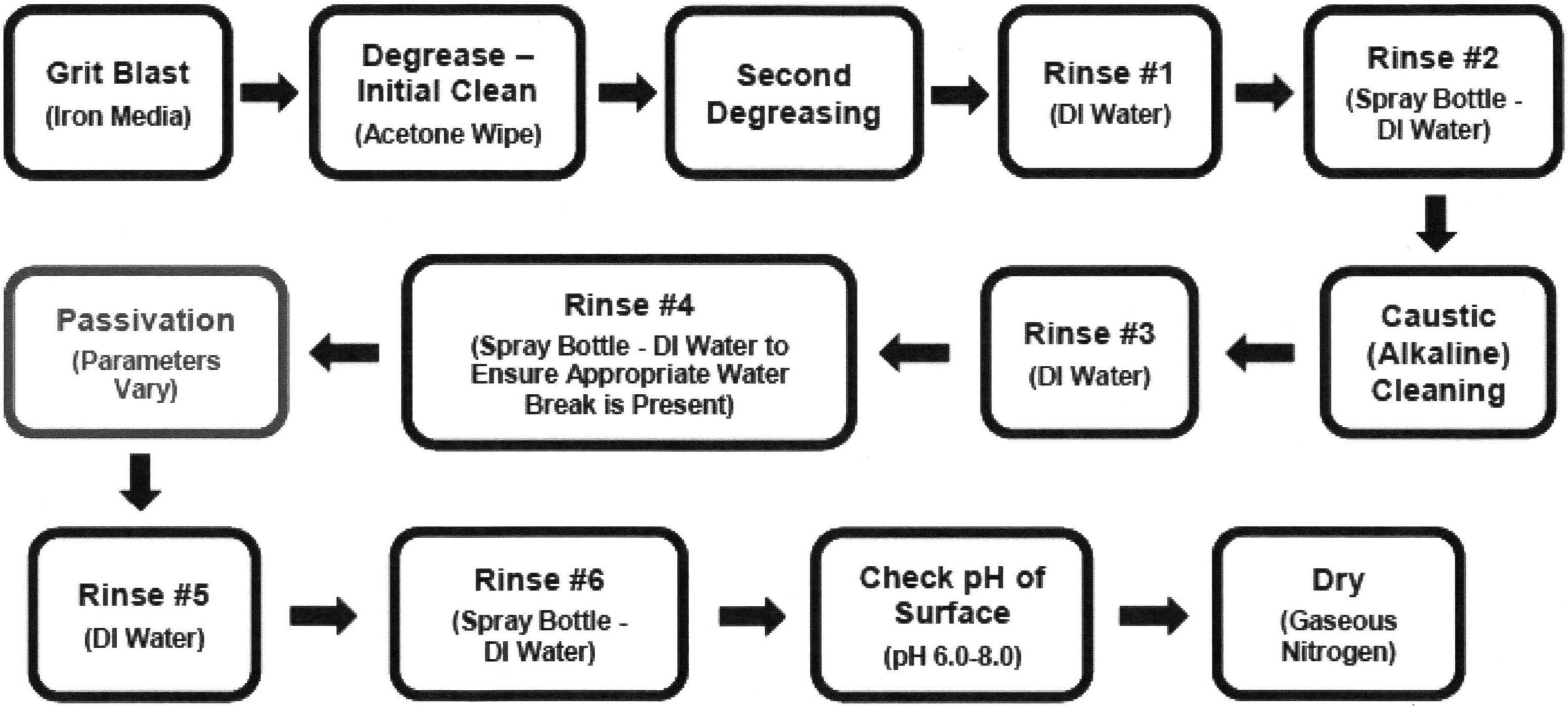
Experimental Procedure

Stainless Steels Alloys of Interest		
Type	**Alloy**	**UNS Number**
Super Austenitic	AL-6XN	N08367
200 Series Austenitic	A286	S66286
300 Series Austenitic	304	S30400
300 Series Austenitic	316	S31600
300 Series Austenitic	321	S32100
400 Series Martensitic	410	S41000
400 Series Martensitic	440C	S44004
Precipitation-Hardened Martensitic	15-5PH	S15500
Precipitation-Hardened Martensitic	17-4PH	S17400
Precipitation-Hardened Martensitic	17-7PH	S17700

Experimental Procedure

Performance Requirements		
Test	**Acceptance Criteria**	**References**
Parameter Optimization	Best parameters	ASTM B 117 and D 610
Tensile (Pull-off) Adhesion	Alternative performs as well or better than control process	ASTM D 4541
X-Cut Adhesion by Wet Tape		ASTM D 3359
Cyclic Corrosion Resistance		GMW 14872
Atmospheric Exposure Testing		ASTM D 610 and D 714 and NASA-STD-5008
Stress Corrosion Cracking		ASTM E 4, E 8, G 38, G 44 and MSFC-STD-3029
Fatigue		ASTM E 466
Hydrogen Embrittlement		ASTM F 519
Liquid Oxygen (LOX) Compatibility	Twenty samples must not show any reaction when impacted at 98 J.	NASA-STD-6001

Test Specimen Preparation



Passivation procedures varied by alloy.

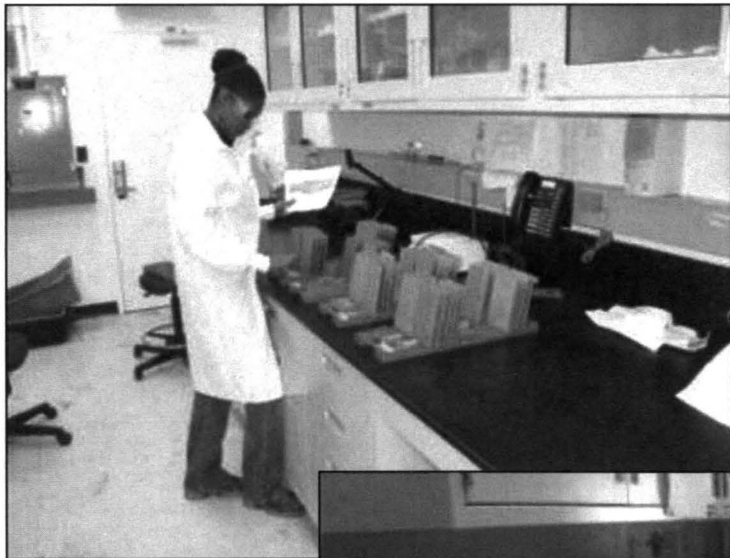
Experimental Procedure

Due to the uncertainty of funding during project development, the testing was divided into three (3) stages.

	AL-6XN	A286	17-4PH	304	316	321	410	440C	15-5PH	17-7PH
Parameter Optimization	1	1	1	1	3	3	3	3	3	3
Tensile Adhesion	1	1	1	1	3	3	3	3	3	3
Atmospheric Exposure	1	1	1	1	3	3	3	3	3	3
Stress Corr Cracking	1	1	1	1	3	3	3	3	3	3
X-Cut Adhesion	2	2	2	2	3	3	3	3	3	3
Cyclic Corr Resistance	2	2	2	2	3	3	3	3	3	3
Fatigue	N/A	N/A	3	3	3	3	3	3	3	3
Hydrogen Embrittlement	3									
LOX Compatibility	Complete—all samples passed testing per NASA-STD-6001									

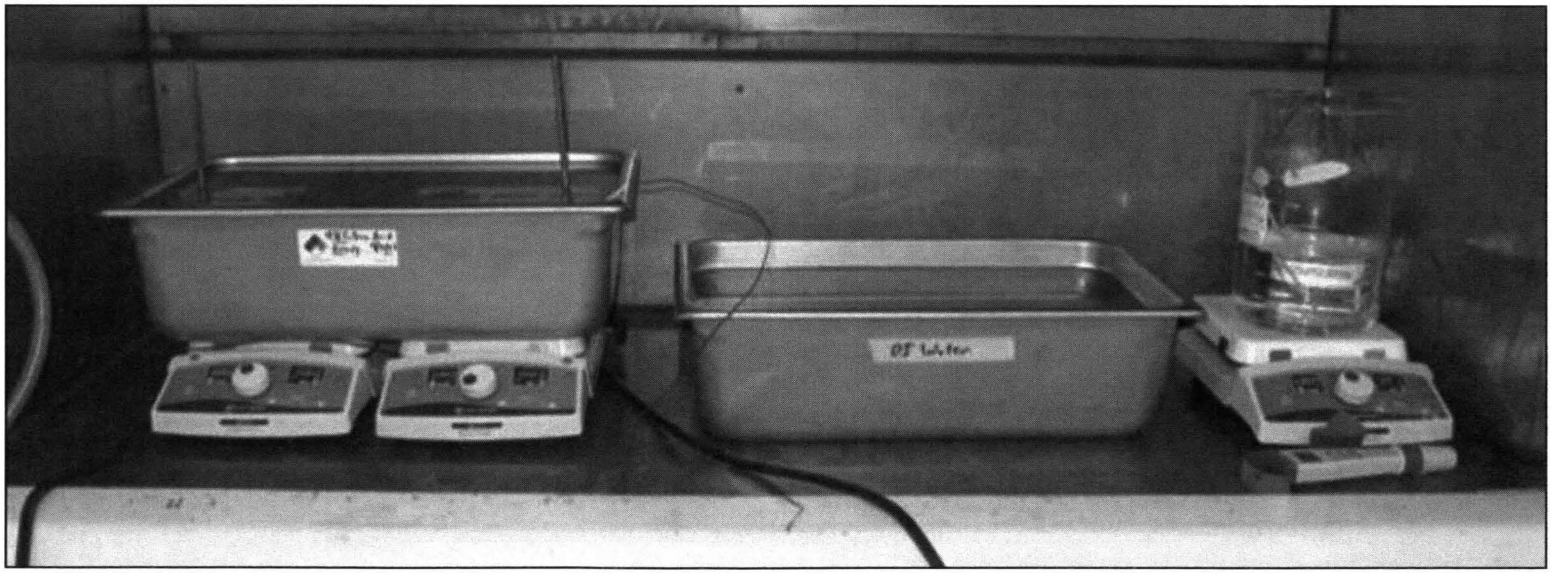
Testing Summary

- **Stage 1 Testing is currently underway.**
- **Stage 1 Alloys:**
  - UNS N08367
  - UNS S66286
  - UNS S30400
  - UNS S17400
- **Stage 1 Tests:**
  - Parameter Optimization
  - Tensile (Pull-off) Adhesion
  - Atmospheric Exposure
  - Stress Corrosion Cracking
- **Results presented are to-date**

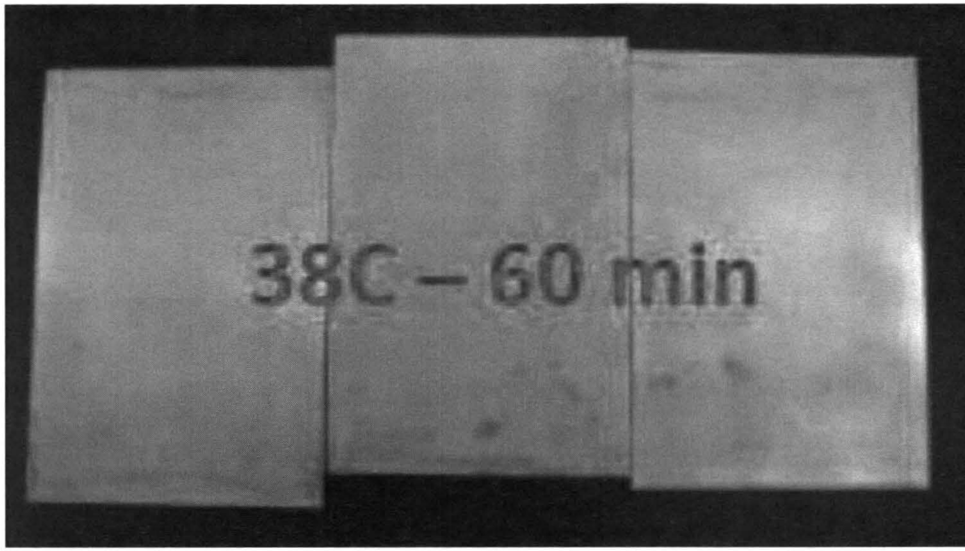


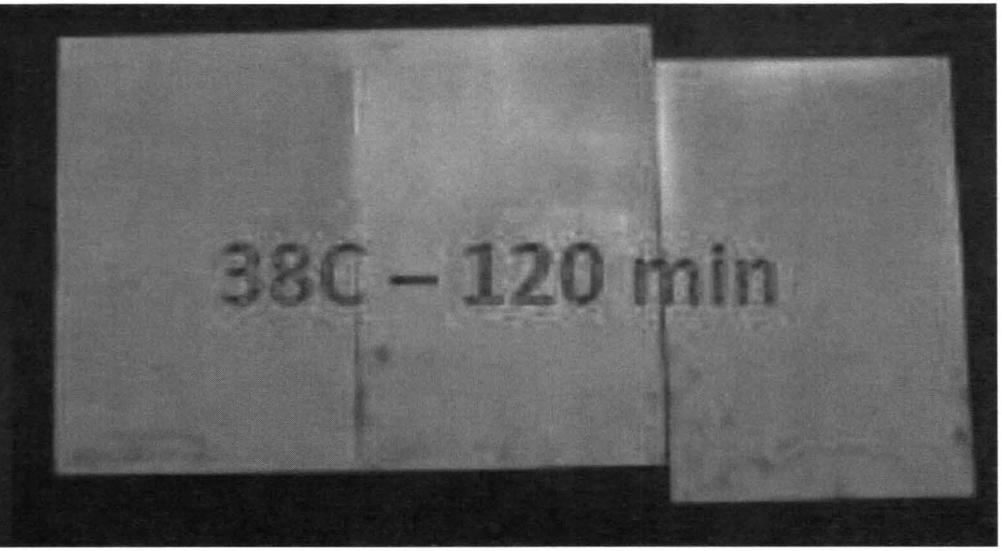
Parameter Optimization – UNS S66286

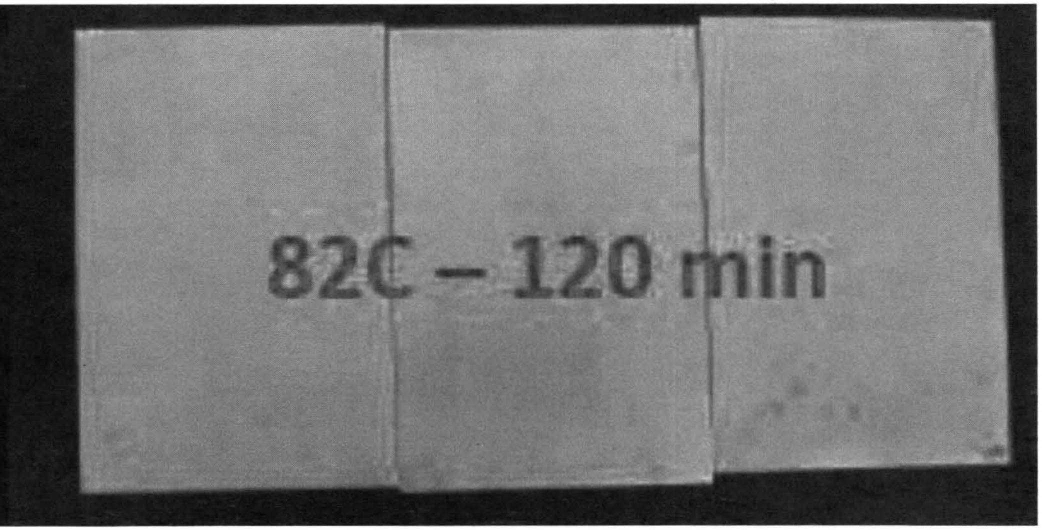
- **After 504 hours, it appeared that *processing time had little effect* on the corrosion related discoloration on the surface.**
  - The 60-minute and 120-minute processing times exhibited little difference in appearance at 38 °C.
- **Conversely, the *higher processing temperatures showed a reduction in discoloration* in comparison to the panels processed at 38 °C.**
  - But there was little difference between 60 and 120 minutes.



Parameter Optimization – UNS S66286



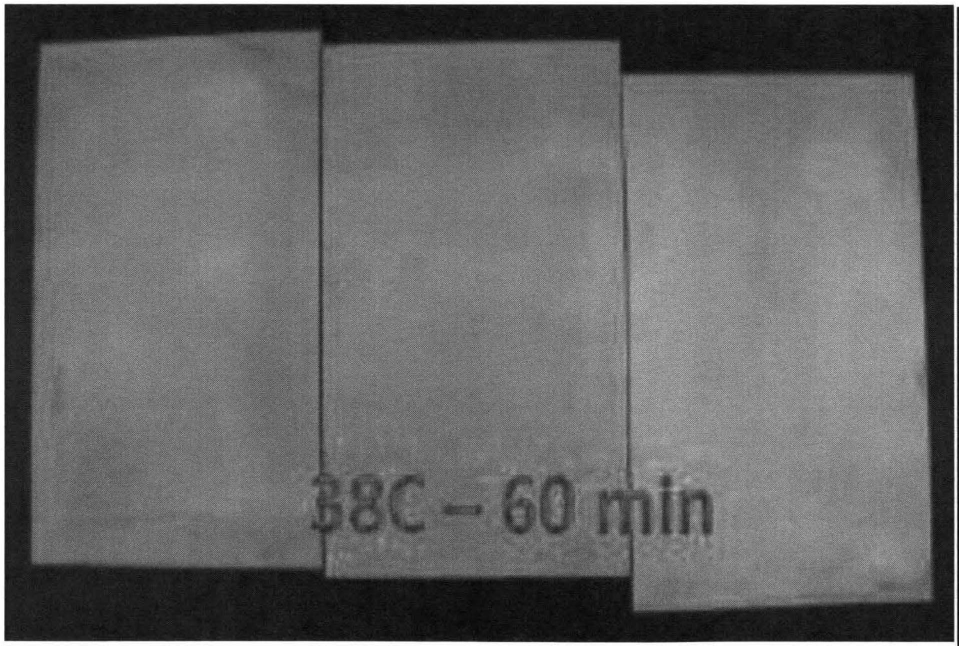


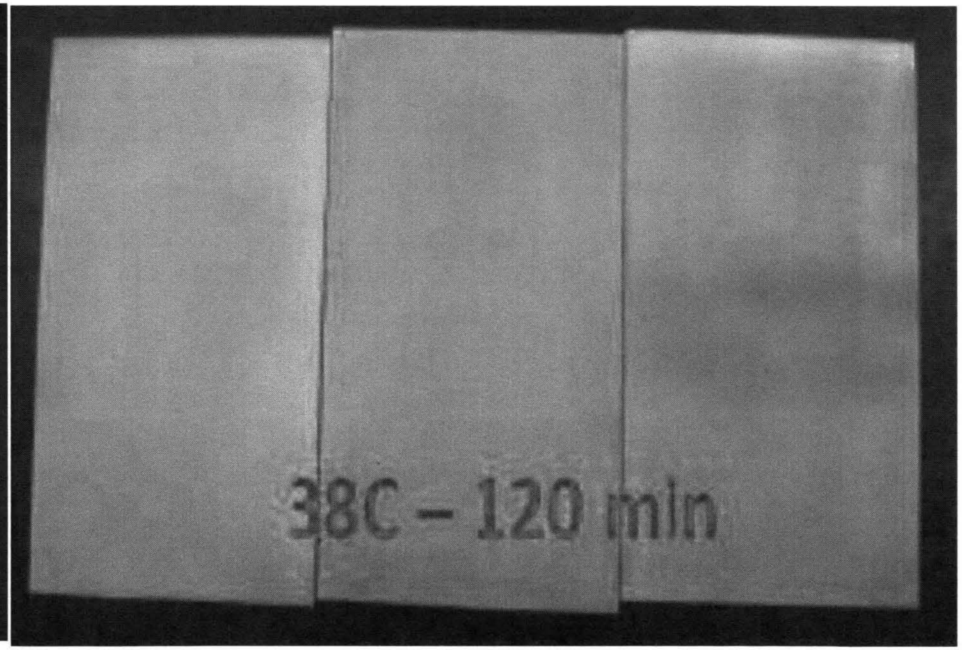


Selected Parameters: *82 °C and 60 minutes*

Parameter Optimization – UNS S08367

- **After 504 hours, *no distinguishable differences* in the corrosion performance as a function of time or temperature were evident.**
  - Consideration was given to USA testing for UNS S30400 (also an austenitic stainless steel) indicating that 120 minutes showed better corrosion performance.





Selected Parameters: *38 °C and 120 minutes*

Parameter Optimization

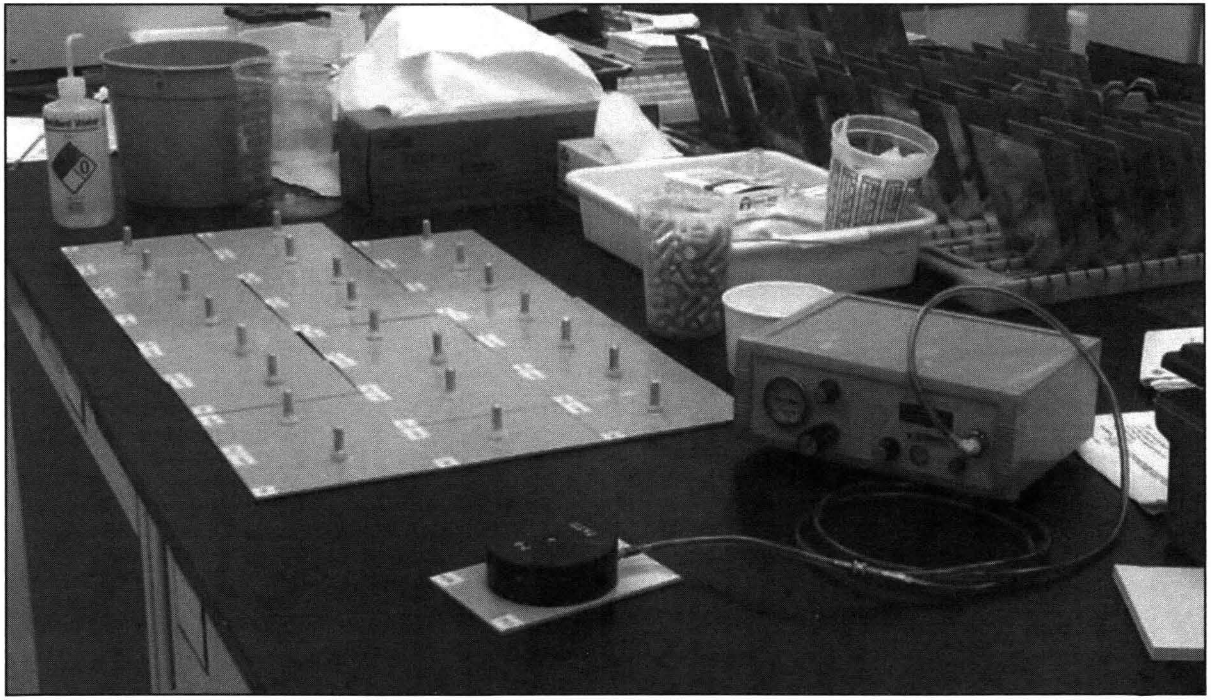
The following parameters were used for the preparation of Stage 1 test specimens.

Alloy	Passivation	Concentration (%)	Bath Temperature (°C)	Time (minutes)
UNS N08367	Nitric Acid	22.5	66	20
	Citric Acid	4	38	120
UNS S66286	Nitric Acid	50	64	30
	Citric Acid	4	82	60
UNS S30400*	Nitric Acid	22.5	66	20
	Citric Acid	4	49	120
UNS S17400*	Nitric Acid	50	64	30
	Citric Acid	4	38	30

*** Citric acid processing parameters determined during USA testing**

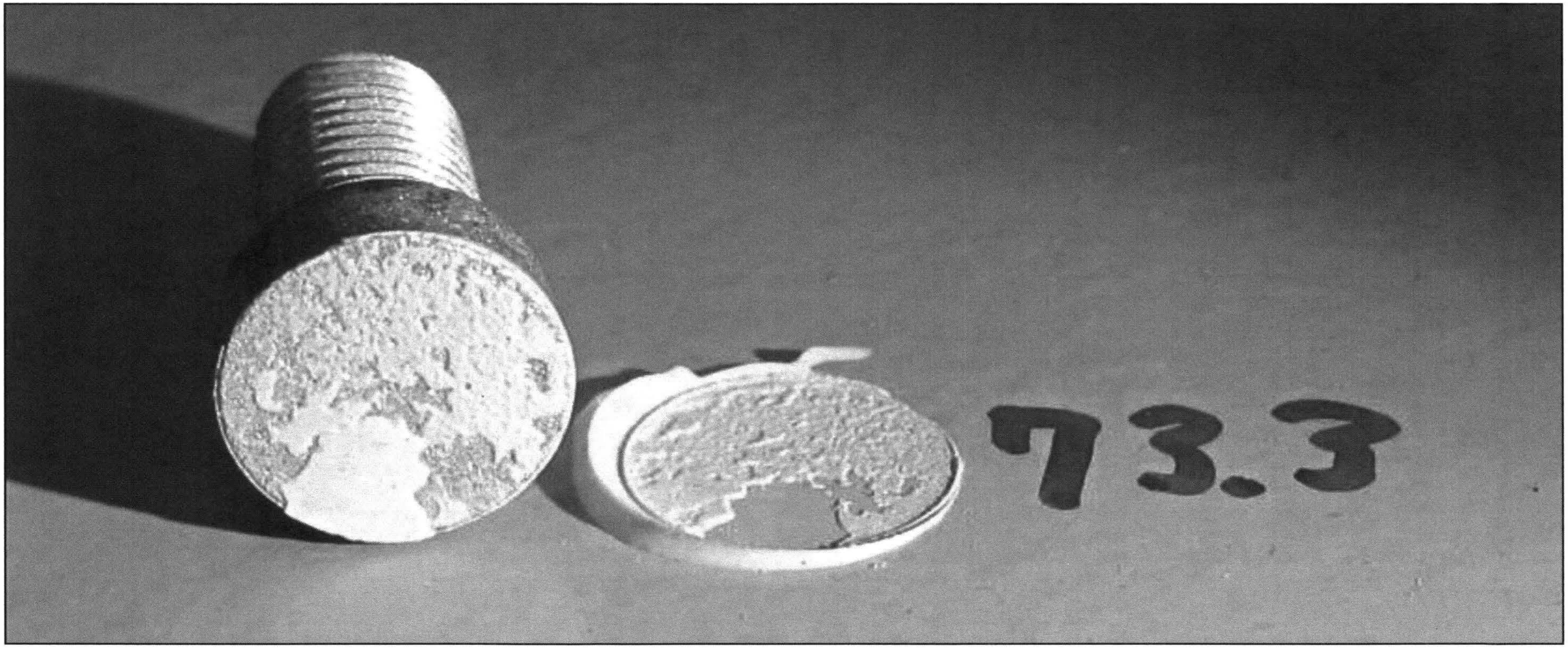
Tensile Adhesion

- **Adhesion values were determined using a PATTI adhesion tester per ASTM D 4541.**
  - Liquid primers from Approved Products List in NASA-STD-5008 were used.
  - Dollies were affixed to the panel surface and allowed to cure for 24 hours.
  - Testing instrument gives a burst pressure value, which is converted to an adhesion value (PSI).



Tensile Adhesion

- Except for 2 nitric acid passivated panels, all pull-off values were strictly related to the epoxy adhesive.



Conclusion: ***There is no evidence that citric acid is detrimental to adhesion.***

Tensile Adhesion

System	Burst Pressure	PSI	Average PSI	Failure Mode	Relative % Difference
UNS S30400 Citric	61.1	2488	2550	100% Glue	10
	71.4	2909		100% Glue	
	65.6	2672		100% Glue	
UNS S30400 Nitric	66.5	2709	2561	100% Glue	18
	50	2035		100% Glue	
	55.6	2264		100% Glue	
UNS S17400 Citric	62	2525	2550	100% Glue	4
	66	2688		100% Glue	
	63.8	2599		100% Glue	
UNS S17400 Nitric	55.5	2260	2231	100% Glue	4
	52.5	2137		100% Glue	
	53.4	2174		100% Glue	

Relative % Difference = Percentage difference between values for each alloy/passivation set

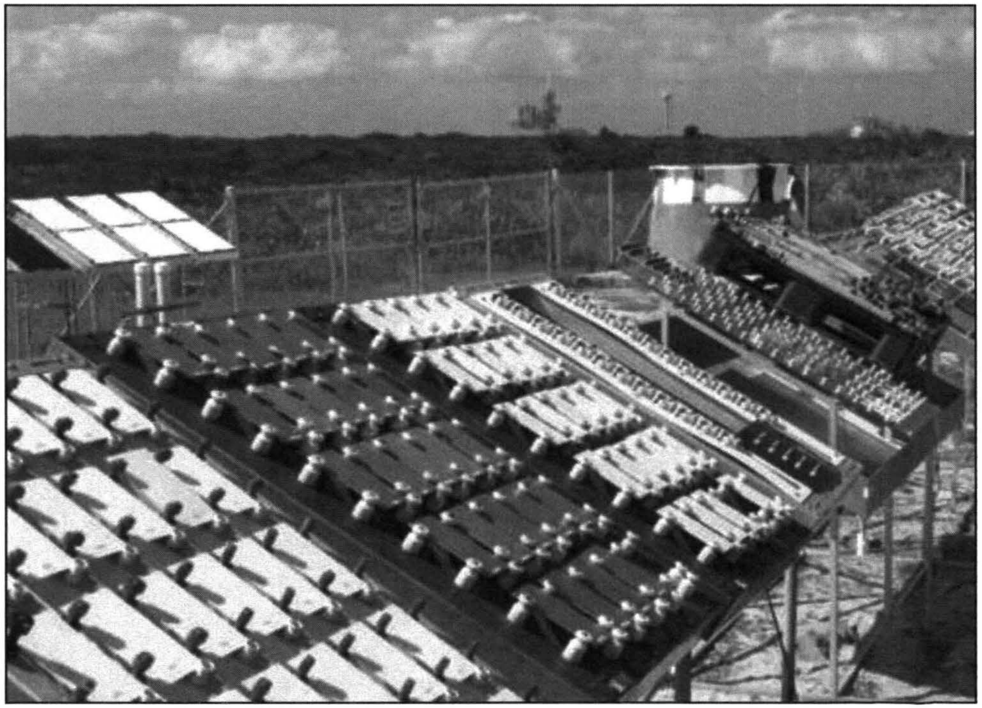
Tensile Adhesion

System	Burst Pressure	PSI	Average PSI	Failure Mode	Relative % Difference
UNS N08367 Citric	42.7	1737	2101	100% Glue	29
	58.6	2386		100% Glue	
	69.4	2827		100% Glue	
UNS N08367 Nitric	75.8	3088	2969	95% Glue – 5% Primer	10
	64.8	2639		95% Glue – 5% Primer	
	67	2729		100% Glue	
UNS S66286 Citric	73.3	2986	2731	100% Glue	19
	61.4	2501		100% Glue	
	54.5	2219		100% Glue	
UNS S66286 Nitric	36.4	1480	1671	100% Glue	27
	57	2321		100% Glue	
	50.4	2052		100% Glue	

Relative % Difference = Percentage difference between values for each alloy/passivation set

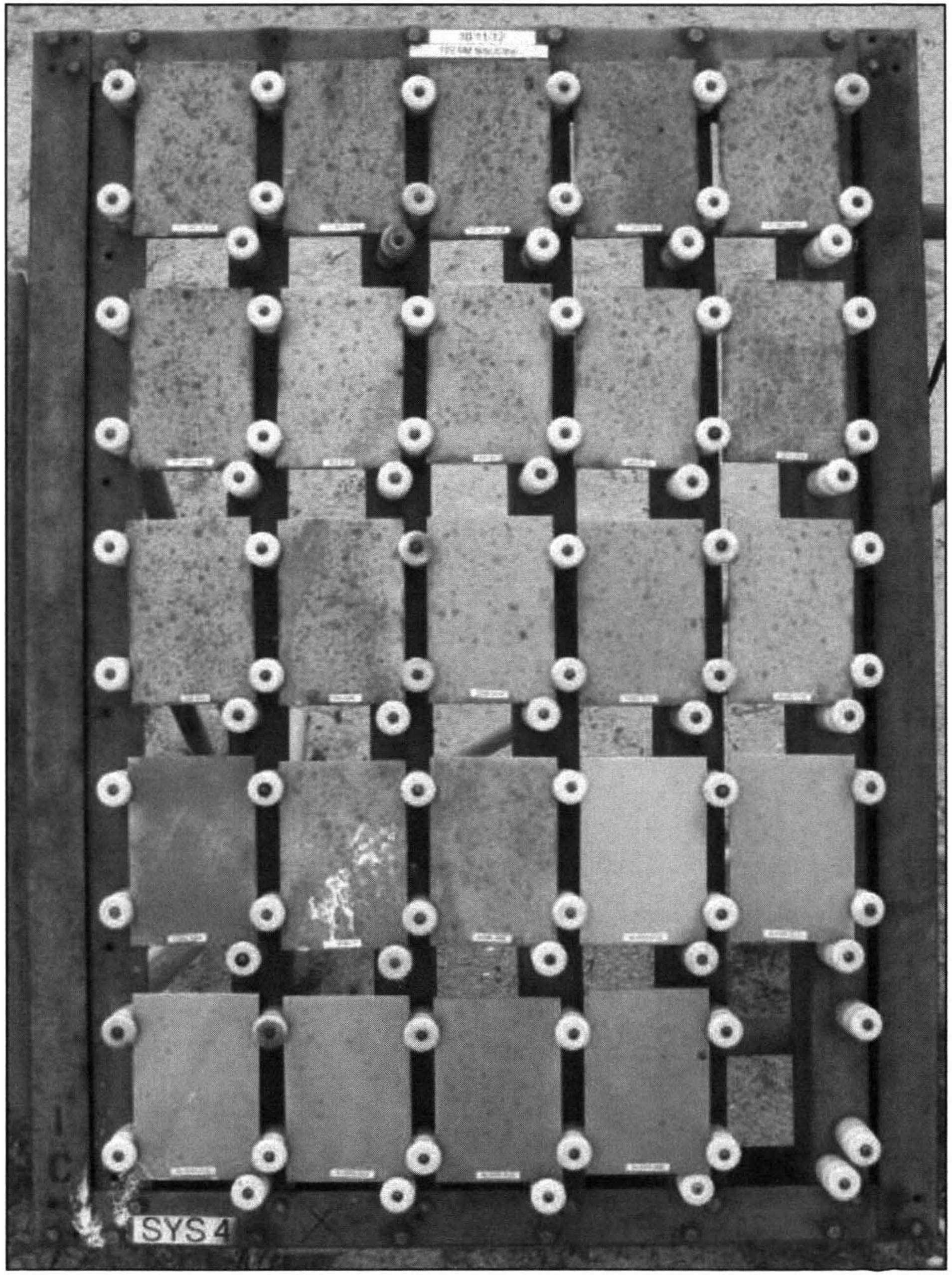
Atmospheric Exposure Testing

- **Test panels were placed at the KSC Beachside Atmospheric Test Facility.**
  - Test racks located approximately 150 feet from Atlantic Ocean high tide line.
- **Panels were evaluated according to visual standards in ASTM D 610 and converted from the degree of observation to a rust grade.**
- **Test specimens included:**
  - Nitric/Citric Acid Passivated-only
  - Nitric/Citric Acid Passivated-Coated (primer + topcoat)
- **Exposure was initiated on 10/11/12.**



Atmospheric Exposure Testing

- Test panels were evaluated at 1, 3, and 6 months.
- Passivated-Coated Panels: *No signs of corrosion were evident on either* the citric acid passivated or nitric acid passivated panels.
- Passivated-only Panels: Citric acid passivated panels exhibited *equal to, or better than, corrosion performance* when compared to the nitric acid passivated panels.



Atmospheric Exposure Testing

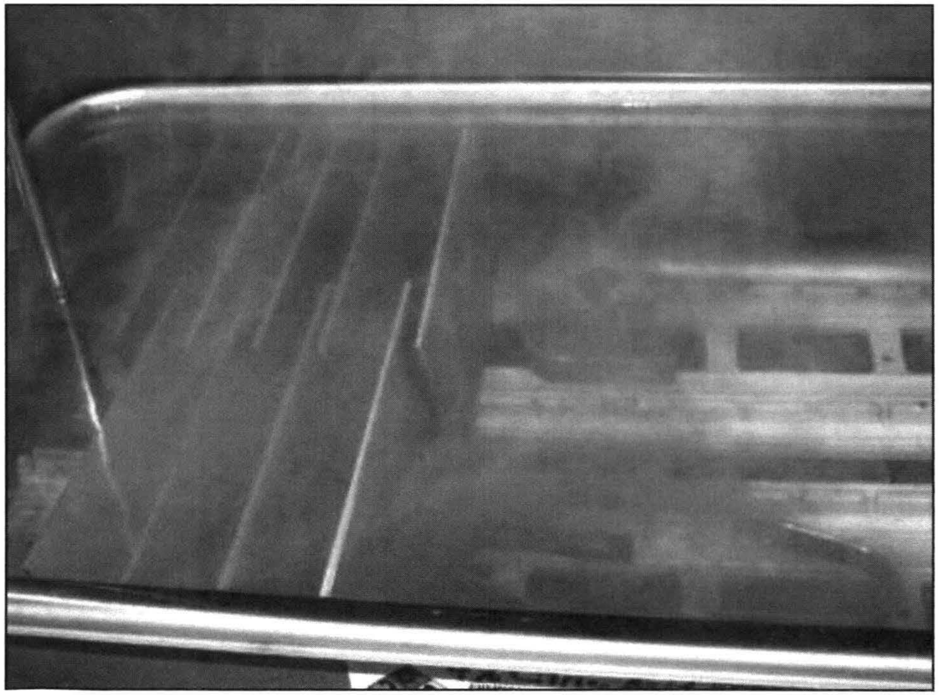
Alloy	Passivation	1 Month Ranking	3 Month Ranking	6 Month Ranking
UNS N08367	Citric	10	10	10
	Citric	8	7	7
	Citric	8	8	7
	Nitric	8	8	7
	Nitric	6	6	6
	Nitric	8	8	7
UNS S66286	Citric	6	5	5
	Citric	6	5	5
	Citric	6	5	5
	Nitric	3	1	1
	Nitric	6	5	4
	Nitric	6	5	4

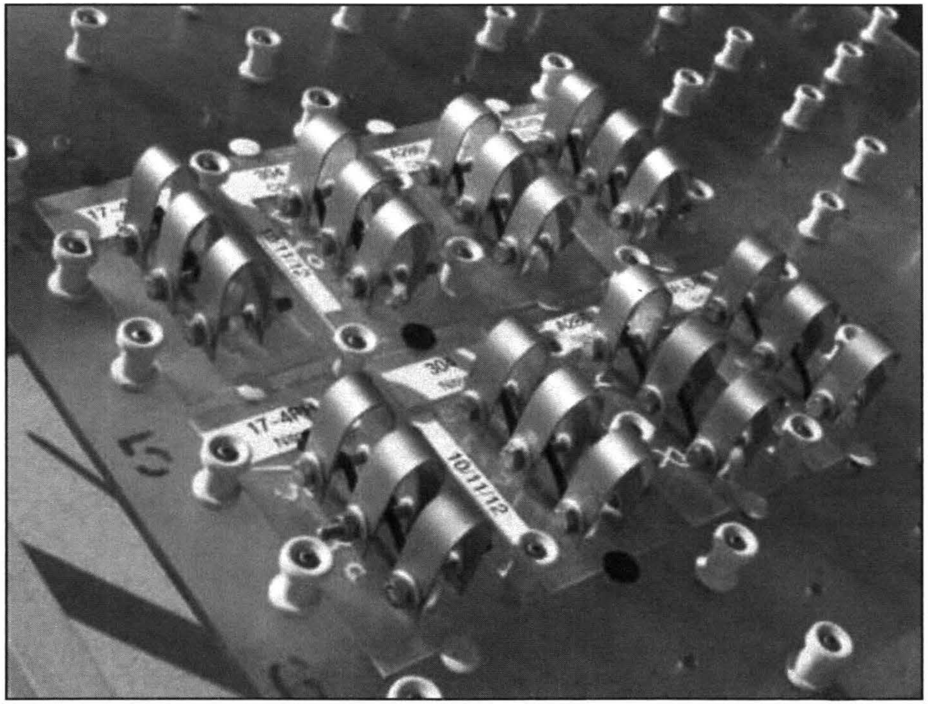
Atmospheric Exposure Testing

Alloy	Passivation	1 Month Ranking	3 Month Ranking	6 Month Ranking
UNS S30400	Citric	5	5	3
	Citric	5	5	3
	Citric	5	5	3
	Nitric	4	4	2
	Nitric	4	4	2
	Nitric	4	4	2
UNS S17400	Citric	4	3	3
	Citric	4	3	3
	Citric	4	3	3
	Nitric	3	3	2
	Nitric	4	3	3
	Nitric	4	3	3

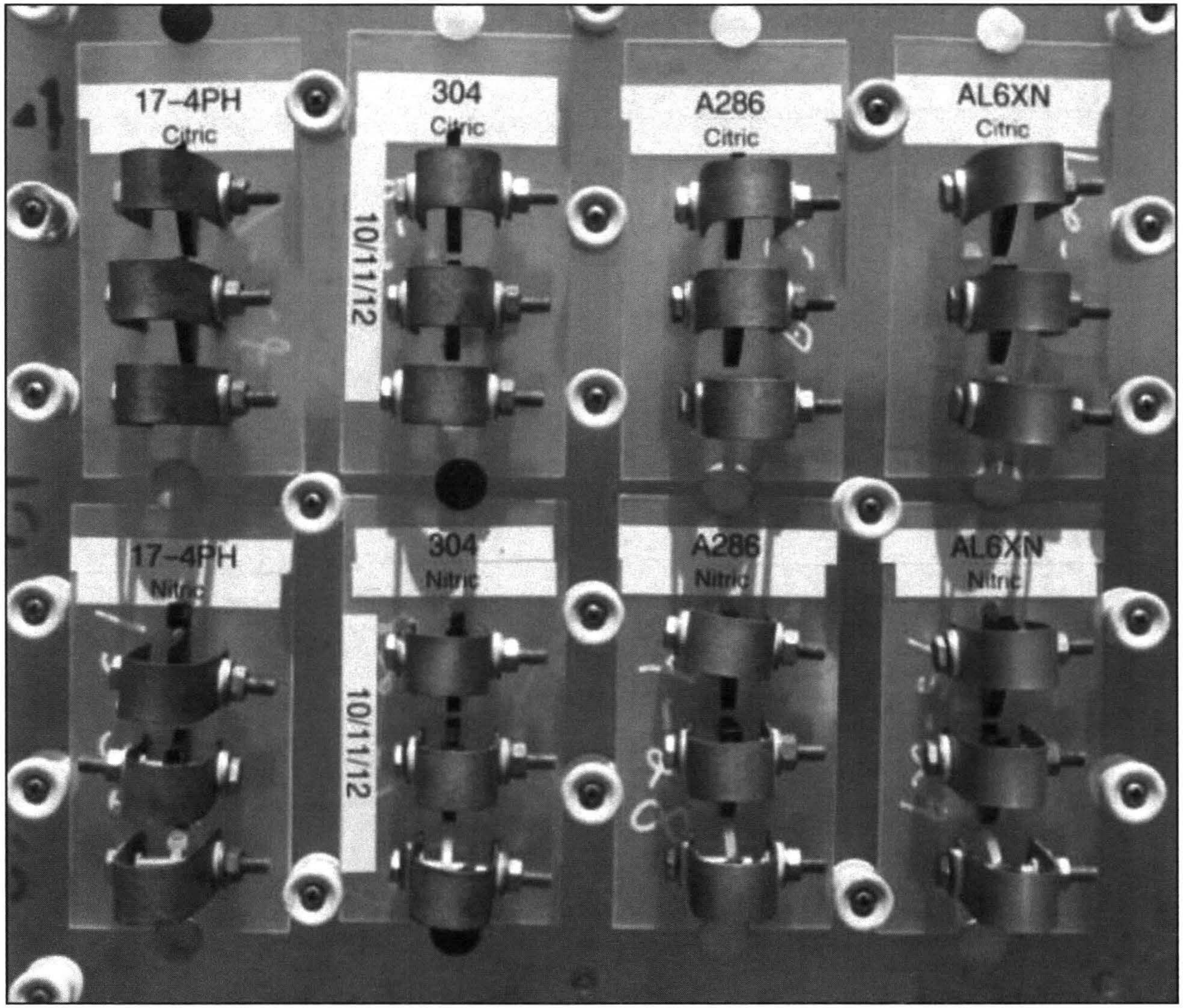
Stress Corrosion Cracking

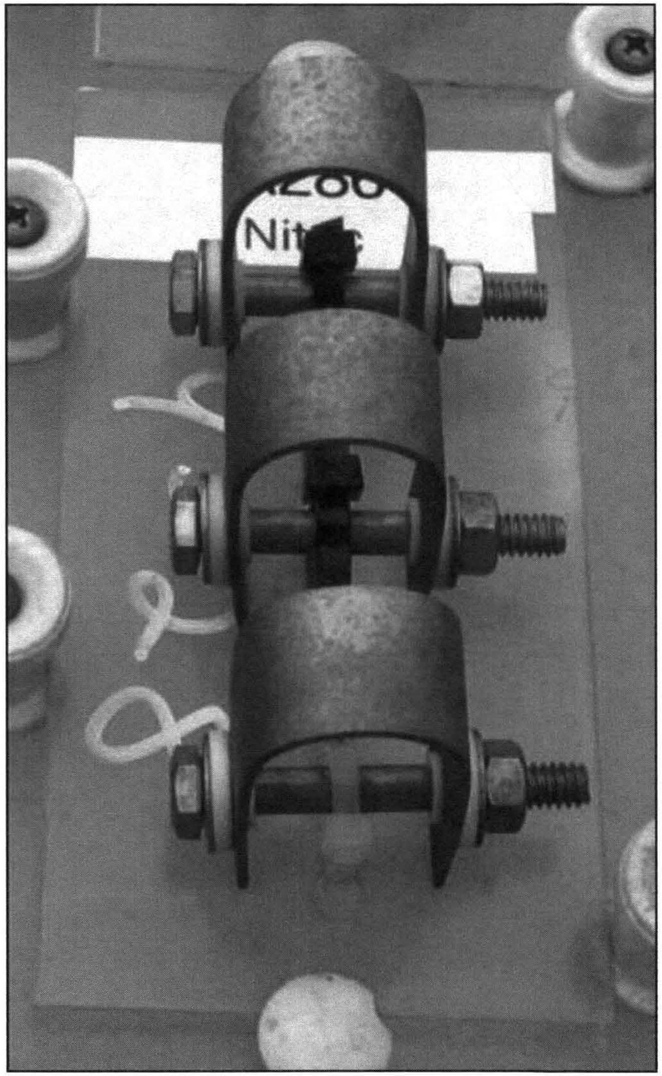
- **Stress corrosion cracking can lead to sudden failure of normally ductile metals subjected to a tensile stress.**
  - Test specimens meeting ASTM G 58 were passivated alongside flat panel specimens.
  - After passivation, samples were stressed and placed at the KSC Beachside Atmospheric Test Facility.
- **Exposure was initiated on 10/11/12.**





Stress Corrosion Cracking





After 6 months of exposure, there has been no evidence of cracking on any specimens.

Conclusions

- **Parameter Optimization**
  - Process parameters were determined for Stage 1 alloys not included in the USA study.
- **Tensile (Pull-off) Adhesion**
  - The citric acid passivation had no derogatory effect on the adhesion of a liquid primer.
- **Atmospheric Exposure (after 6 months)**
  - There is no evidence of corrosion on any of the Passivated-Coated panels.
  - The citric acid passivated-only panels had an equal or lesser degree of corrosion when compared to the nitric acid passivated-only panels.
- **Stress Corrosion Cracking**
  - No samples have cracked after 6 months of exposure.

At this point, it appears that citric acid performs as well as, or better than, nitric acid.

Future Work

- **Stage 1 Testing continues.**
- **Stage 2 and Stage 3 Testing has recently started and includes the other identified alloys and additional tests:**
  - X-Cut Adhesion by Wet Tape
  - Cyclic Corrosion Resistance
  - Fatigue Testing (selected alloys)
  - Hydrogen Embrittlement
- **Place test panels at Guiana Space Centre for comparative atmospheric exposure testing.**

Project Sponsors

- NASA HQ Environmental Management Division
- NASA Ground Systems Development and Operations (GSDO) Program

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For more information visit the NASA TEERM Website:

http://www.teerm.nasa.gov/AltNitricAcidPassivation.htm